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Annual Summary Report No 3

Experimental Study of Chemi-Ionization in Flames

A REVIEW

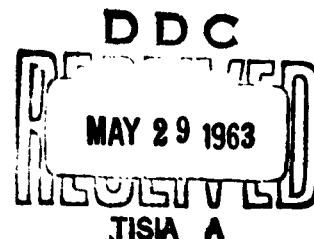
A. VAN TIGGELEN

Professor at the University of Louvain (Belgium)

with the collaboration of

J.N. Bertrand and A. Feugier

May 1963



„The research reported in this document has been sponsored by the Office of Scientific Aeronautical Research Laboratory, OAR, through the European Office, Aerospace Research, United States Air Force.”

Laboratory for Inorganic Chemistry

UNIVERSITY OF LOUVAIN

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ABSTRACTS

This annual report contains together with previous results some recent observations and a complete discussion of the work achieved in the laboratory during the last three years.

1. Description and discussion of two new methods for the determination of the ion concentration in the flame reaction zone (excluding the region of burned gases) by measurements of the electrical conductivity of the flame front.
2. Mass-spectrometry method of identification of the ions which can be extracted from a flame. Complete description of the equipment and summary of the most significant results.
3. Discussion of the problem of the primary process in the production of chemi-ions in the burning zone of a flame. This discussion is based on the observations which have been made not only on oxygen supported flames but also on mixtures of different fuels with nitrous oxide.

INTRODUCTION

It has been thought useful to summarize and to discuss in this report the experimental results which have been obtained in our laboratory during the three last years. The reason for presenting this review is to be found in the fact that our research will take a new direction in the near future; furthermore this document is about the paper which has been presented at the American Rocket Society Meeting in Palm Springs from 10 to 12 October 1962. Only a few supplementary arguments have been added concerning the mechanism of ion formation in flames, some parts of this document are taken from our last Annual Report No 2 (May 1962); this duplication has been judged unavoidable for a good understanding of our review. During this last period of one year a very profound modification of our experimental equipment has been achieved and this of course, was an obstacle to the normal progress of our investigations.

A comprehensive study of ionization processes in flames comprises the solution of three main problems :

1. The elaboration of an adequate method to measure the amount of ionization in the very reaction zone of the flame.
2. The identification of the ions which are formed in the flame front and which are very rapidly disappearing (by recombination) in the burnt gases.
3. The determination of the process of ion formation, taking as an undisputed fact that such process occurs by chimionization in unseeded flames.

The object of this document is to resume the work which has been done in our laboratory on this subject the last years. The research work

resumed here has been more extensively described in previously published papers and in a few United States Air Force Contract Reports (ref 1 to 10) to which we shall refer for more details, concerning the equipment and the measurement techniques.

I. MEASUREMENT OF ION CONCENTRATION IN FLAMES

Some difficulties are encountered in the experimental measurement of ion concentration in flames, and no general method has been proposed which could be applied to any kind of flame.

The method of flame deflection in an external electric field (11) (12) (13), involves a rather complex interpretation of results; the latter are perhaps affected by the alteration of burning velocity (14). The microwave attenuation method gives very variable data concerning equilibrium and ionization processes in flames and it has been successfully applied by T. M. Sugden and coworkers (15); the method however requires a minimum volume (dimension at least equal to the wavelength) and is therefore not appropriate to the investigation of the flame front itself except, perhaps, in the case of very low pressure flames.

Finally the use of Langmuir probes (16) (17) is able to give interesting data on the distribution of ions in the flame.

This method has shown that the chemiionization is located in the flame front; however the exploration of the flame front itself can only be made on very low pressure flames where the flame front thickness exceeds the probe dimensions.

In any case the method is restricted to the investigation of flames with a temperature low enough to make the thermoemission of the probe (generally Platinum wire) negligible as compared to the ion concentration of the flame.

However it has been possible to maintain the principle of the probe method but to modify profoundly the modalities of its application in view of determining the conductivity of the reaction zone in the flame. Successively two different ways have been followed.

A. Method of the circular slit burner

(with the collaboration of J. Poncelet (4) (5))

In order to avoid the limitations and difficulties encountered in the conventional probe method, a technique has been elaborated which fulfills the following requirements :

- it should enable us to measure exclusively the ionization in the flame front (excluding the burnt gases)
- it should be applicable even to very hot flames
- it should not perturb the flame front by quenching effect.

All these conditions seem to be achieved in the method of the circular burner for which a schematic representation is given in figure 1 and 2.

The current intensity flowing through the flame is the only measurement to make when applying a potential drop between the inner and outer burner tube. The necessary equations will be briefly repeated here :

$$i = \frac{E}{R_a + R_f + R_c} \quad (1)$$

i = current intensity

E = potential applied between the inner and outer tube

R_a and R_c = contact resistance at anode and cathode

R_f = flame resistance

$$R_f = \frac{\rho l}{L x_o} \quad (2)$$

ρ = specific resistance of flame

l = length of flame (see figure 2)

L = perimeter of annular flame = $2\pi r$

x_o = thickness of flame front

$$V_o = \frac{D}{S} = \frac{D}{2\pi r l} \quad (3)$$

D = gas flow

S = flame surface

V_o = burning velocity

By substitution of (2) and (3) in (1), one obtains :

$$\frac{1}{i} = \frac{R_a + R_c}{E} + \frac{\rho D}{(2\pi r)^2 V_o x_o E} \quad (4)$$

From theoretical considerations on burning velocities and from experimental facts it has been shown that (18)

$$V_o x_o = 0.96 \times 10^{-2} \sqrt{T_m} \quad (5)$$

T_m = mean flame temperature (19) = $T_i + 0.74 (T_f - T_i)$

T_f = flame temperature (final)

T_i = initial temperature of fresh gases

Equation (4) becomes now :

$$\frac{1}{i} = \frac{R_a + R_c}{E} + \frac{\rho D}{10^{-2} 0.96 (2r)^2 E \sqrt{T}} \quad (6)$$

If we suppose that R_a and R_c remain constant when the gas flow increase, ρ can be derived from the slope of a plot of $1/i$ against gas flow D .

$$\text{Since } \frac{1}{\bar{p}} = n e (k+ + k-) \quad (7)$$

e = charge of electron

k_+ and k_- = mobility of positive ion and electron

$$k_- = 2500 \text{ cm/sec} \ggg k_+$$

So finally we obtain n = number of ions per cc

The method of measuring the concentration of the ions present in a flame, as described here above, has been applied to a few different kind of mixtures (containing a given oxidant and a given fuel).

It has been definitely shown that for a given degree of dilution the maximum ion concentration coincides very nearly with the maximum burning velocity (4) (5). Furthermore a very rough estimation of the activation energy of the process of the ion formation shows that it varies between very broad limits around 50 to 100 kcal for widely different fuels mixed with oxygen but that it does not exceed 150 kcal (4) (5) (8).

The apparent activation energy being calculated graphically from a plot of $\log (n T_m / Y)$ against $1/T_m$ according to (4) for mixtures with constant ratio fuel to oxidant but increasing dilution with nitrogen :

$$\log (n T_m / Y) = K - \frac{E \log e}{R T_m} \quad (8)$$

where $Y = \frac{100 - \% \text{ inert gas}}{100}$ (taking the dilution into account).

The calculated values of the activation energies prove definitely that any possibility of thermal ionisation is excluded since all reasonable values of ionisation are about $10 \text{ eV} \approx 230.000 \text{ calories}$.

Lastly it will be noted that the order of magnitude of ion concentration in stoichiometric hydrocarbon-air mixtures has been found equal to about $10^{10}/\text{cc}$ by this method.

B. The rectangular slit burner method

(with the collaboration of H. Philippaerts (10))

The theory of the conductivity of ionized flame gases has been elaborated by H. Wilson (20) : he considered the potential distribution between two plane and parallel electrodes along a hot gas where a steady concentration of ions and electrons is maintained by a process of ion formation which compensates the losses by recombination. The total potential applied to the electrodes V can be considered as a sum of three terms :

$$V = V_a + V_f + V_c$$

where V_a and V_c represent the anodic and cathodic drop while V_f corresponds to the potential drop in the flame itself where a constant electric field is assumed.

The current intensity is proposed by Wilson to obey the following equation

$$V = A_i^2 + Bid$$

d = distance between the two electrode plates, A and B are constants for a given flame and given electrodes.

The term Bid should then be equal to V_f ; this means that Ohm's law is obeyed in the flame, at least as long as the applied potential does not reach prohibited high values.

The term Ai^2 corresponds to the potential drop near the electrodes as a result of a phenomenon of space charging.

Evidently the specific resistivity of the flame should be obtained by the ratio of B to the transversal section of the flame. The relation between V and i allows to obtain B by plotting V/i versus i since the intercept of the straight line on the ordinate axis would be equal to Bd ;

indeed :

$$\frac{V}{i} = B_d + A_i$$

We have repeatedly tried to use this equation and the corresponding plots in order to measure the flame resistance without any success (uncoherency of experimental results) and it is our belief that the equation proposed by Wilson is only approximative.

The new method which is presented in this section is essentially based on the equation $V = V_a + V_c + V_f$ presented hereabove; it differs essentially from the conductivity method proposed earlier in this laboratory and described in the preceding section by the important improvement that it is no more based on the assumption that the dead space near the electrodes does not depend on the gas flow feeding the "circular slit burner" used previously. It has been observed indeed that this assumption is not correct and that the method does not allow the measurement of the conductivity of the flame itself but that it rather consists in the measurement of the cathodic potential drop.

As a consequence all previously ion concentrations obtained by the circular slit burner technique are not correct; it will be shown that the true values are higher than proposed previously.

1. Description of experimental equipment :

The burner is schematically described in figure 3 A. The laminar premixed flame is burning on a slit of about 0.1 cm broadness and a length equal to 24.5 cm. The water jacket takes care of an efficient cooling of the upper part of the burner.

The two electrodes (figure 3 B) were made of massive bridge shaped copper pieces; they are cooled by sucking a strong air current through a cylindrical boring which passes through the metal. A small hole pierced just above the burner slit allows the elimination by suction of

the flammable gases which would otherwise cause a deformation of the flame against the electrode. This device allows the gas profile to be uniform not only between the electrodes but even right to the space contact between the flame and the electrodes. The latter can be moved at a variable distance from each other by means of a fine adjusted screw system.

2. Theoretical considerations :

The potential applied V to two electrode plates is given by :

$$V = V_a + V_c + \rho \frac{i d}{S}$$

ρ = specific resistivity of the flame ($V_f = \rho i d/S$)

S = tranverse section of the flame (parallel to electrodes)

d = distance between electrodes

Since the ion concentration in the burnt gases is much smaller than in the flame front itself it may be assumed that (fig. 3 C)

$$S = x_o l$$

x_o = flame front thickness

l = length developped by the flame front above the slit.

Furthermore the burning velocity V_o is given by :

$$V_o = \frac{D}{L \Gamma}$$

L = total length of the slit

D = total gas flow of flammable mixture feeding the burner.

By combination of the three last equation we obtain :

$$V = V_a + V_c + \rho \frac{i L V_o d}{D x_o} \quad (9)$$

Two methods are now possible :

a. If the distance between the two electrodes is changed, the applied potential V can be adjusted in such a manner as to keep the intensity i constant

If the necessary potential V is then plotted versus the electrode distance d , a straight line is obtained with a slope

$$\operatorname{tg} \alpha = \rho \frac{i L V_o d}{D x_o} \quad (10)$$

combining with : $1/\rho = n e k$

where n = ion concentration = electron concentration

e = charge of electron = $1.6 \cdot 10^{-19}$ Cb

: k = mobility of electron = 2500 cm/sec/Volt (20)

we obtain :

$$n = \frac{i L V_o}{k e D x_o \operatorname{tg} \alpha} \quad (11)$$

Since it has been shown (18) that $x_o = 0.96 \cdot 10^{-2} \sqrt{T_m} / V_o$

$$n = \frac{i L V_o^2 \cdot 10^2}{0.96 k e D \operatorname{tg} \alpha \sqrt{T_m}} \quad (12)$$

with $L = 24.5$ cm and taking all constants together

$$n = 6.4 \cdot 10^{18} \frac{i V_o^2}{D \operatorname{tg} \alpha \sqrt{T_m}} \quad (13)$$

i = in amp; V_o in cm/sec; D in cc/sec

T_m = mean temperature of flame front

$$= T_i + 0.74 (T_f - T_i) \quad (19)$$

b. By using two identical probes placed between the two electrodes at a given distance d' from each other the potential drop between the probes divided by d' gives directly the value of $tg\alpha$ from one single measure.

This more simple method presents the advantage that it does not need more than one measurement; it is strictly valid only if the two probes are perfectly identical since the perturbation due to the two probes are exactly compensated under this condition.

The concentrations obtained by the two methods are always in the same ratio : the ion concentration obtained by the first method is always about twice the concentration obtained by the second method; however because of its simplicity the latter has been used to obtain the experimental results given below since we were only interested in the relative values of the ion concentration when the composition of the flammable mixture is changed.

The electrical mounting is schematically given for the two methods respectively in fig. 4 A and 4 B.

The resistance R_t in figure 4 A consists in a serie combination of

12 resistances of	1 M Ω
12 "	of 100 k Ω
12 "	of 15 k Ω
1 variable resistance of	20 k Ω

In the second method the potential drop between the two probes is measured in a Poggendorf system with a potentiometer bridge of 10 k Ω in order to annihilate the current intensity. The zero point instrument consisted in a very sensitive galvanometer while a conductimeter was used to measure the resistance BC (fig. 4 B).

3. Experimental testing of the method :

In order to verify the relation

$$V = V_a + V_c + \frac{p i d}{S}$$

different plots are given of V versus d in figure 5 A for different values of the total potential V_t applied to the electrodes. The observed linearity proves the constancy of V_a and V_c as long as the total potential V_t remains constant; furthermore it can be seen that the total electrode potential drop in the dead spaces at the two electrodes is much larger than in the flame.

The linearity of V_f versus the current intensity i is illustrated in figure 5 B at least as long as the current intensity remains sufficiently low; it will be necessary in the application of the method to work under the conditions where the linearity holds.

C. Brief summary of experimental observations

(with the collaboration of H. Philippaerts and
J. D'Olieslager)

The rectangular slit burner method, described in the preceeding pages, seems to give more reproducible and reliable results than the circular slit burner method. It is to note yet that the results obtained for the concentration of the ions in hydrocarbon-air flames are about 100 times larger. As an illustration some data are presented in figure 6 (the absissce R represents the ratio : $\text{CH}_4/\text{CH}_4 + \text{O}_2$). Furthermore a constant value is obtained now for the activation energies of the formation of the ions when equation (8) is applied to the data of figure 6. The obtained activation energy is about equal to 50 kcalories and it remains constant all over the range of the ratio R (figure 7). The temperatures T_m which have been used are based

on measured T_f temperatures. The value of 50 kcalories is very near to the activation energy of 40 kcal found for the branching process in this flame (21).

Kindred measurements are being continued presently in our laboratory on many different kind of flames. To give an example figure 8 presents the ion concentration in ions per cm^3 in a logarithmic scale for a series of methane nitrous oxide flames. It is premature to draw conclusions yet but some interesting observations have been made on the influence of additives. Some indications of the observed facts are reported elsewhere (10).

We would like also to mention some results obtained in a systematic study of the correlation between the intensities of the different band spectra emitted in a flame and the concentration of radicals (10); although such a correlation exists, and especially between OH emission and ion concentration in hydrocarbon flames, it is difficult to propose yet a correlation between the filiation of the excited radicals and the ions which might be considered as the extreme case of excitation state.

Finally we mention the experimental proof that the ionization of alkali metals in a flame is purely thermal : this has been shown by the fact that, whilst hydrogen-oxygen flames contain a negligible amount of ions, the addition of some Na salt is accompanied both by the formation of Na^+ ions and by the emission of the Na doublet; it has been found that

$$\log \frac{n}{(\text{Na})} = K - \frac{66000}{R T_m}$$

With 66000 calories being very near the energy difference 69000 calories between the ionization and resonance energy of the Na atom (6).

n = Number of ions per cc

(Na) = Intensity of the sodium doublet emission.

II. ION EXTRACTION AND IDENTIFICATION IN A FLAME

In order to determine the nature of the ions which are formed in the flame they are to be extracted from the flame and brought into a high vacuum system where, after separation from the burnt gases, they can be accelerated and projected on to a narrow slit which serves as the entrance slit of a conventional mass spectrometer.

The possibility of the direct identification of the flame ions by means of mass spectrometry has been shown in three short notes (2) and later in a paper presented at the 7th International Symposium on Combustion. Independently and almost at the same period Knewstubb and Sugden (22) (23) published a kindred work using a notably different technique.

Two different versions have been elaborated in our laboratory.

A. Low pressure burning flames (3) (5)

(with the collaboration of J. Deckers and S. De Jaegere)

Since a flame cannot be run at the very low working pressure (10^{-5} mm of mercury) of a mass spectrometer, a sample of the flame gases has to be expanded through a hole and behind the latter the burnt gases have to be pumped away while the ions are kept in a straight beam by means of an electrostatic field maintained by a system of electrodes. If the hole is too narrow most of the ions may lose their charge by collision with the walls, but if the hole is large enough no pumping installation would be sufficient to obtain a satisfactory vacuum.

The equipment which we have built makes it possible to bring the ions from a flame burning at pressures from 3 to 10 cm mercury into an intermediate region at 10^{-2} mm of mercury and from there into a vacuum of 10^{-4} mm of mercury. The passage in the intermediate

region was made as short as possible in order to avoid a randomized redistribution of the initially nearly homogeneous ion velocities.

Figure 9 gives a schematic description of the apparatus. It consists of four chambers : the combustion chamber I, the separation chamber II, the acceleration chamber III and the mass analyzer IV.

The Pyrex combustion chamber I (65 mm diameter) contains the burner; it is connected to a pump and has a side arm for the ignition system of the flame. The burner is a copper tube (30 mm diameter) moving in the chamber through a "simmerring". The polished "lava" bottom of chamber I is pressed against the rotating disc by means of a flexible membrane. The separation chamber II is made of a steel cylinder (diameter 300 mm) closed by two steel plates with a rubber seal. A system of "simmer ring" allows rotation of the disc while a vacuum of 10^{-2} mm of mercury is maintained in this chamber. Single holes in the lava bottom and in the rotating disc are 2 mm in diameter and at a distance of 70 mm from the central axis; the communication between I and II lasts $1/220$ of a second, since the revolution speed is 6 rev/s. The communication between chambers II and III consists of a hole (of 2 mm diameter) in a copper plate, supported for insulation by Plexiglas and fitted with a rubber seal. A vacuum of 10^{-4} mm of mercury is obtained in the acceleration chamber by means of an oil diffusion pump. The separation between chamber III and IV consists of the narrow (1 mm broad and 15 mm high) entrance slit of the mass spectrometer. Both electrostatic and magnetic fields can be modified in order to register the different masses caught on the collector which is placed at the end of the analyzer tube (chamber IV). The total accelerating field is divided between the different electrodes which are represented separately in figure 9. Burner, flame and disc where at the same positive potential and only about ten volts drop was used between the latter and the first accelerating lens L_1 . The resolving power of the system

was only 50 m/ Δ m.

B. Atmospheric pressure burning flames (9) (10)

(with the collaboration of J. N. Bertrand)

The principle of the ion extraction from the flame has not been changed; however since the flame is burning at higher pressure the diameter of the periodically opened hole has been reduced to 0.5 mm. The intermittent opening is obtained by the rotation of a stainless steel disc tightly pressed against a nylon surface (fig. 10 and 11). Other materials have been tried with much less success (such as Lava, Teflon and Aluminium). The friction surface was only a circle of about one square centimeter; no exaggerated heating occurs even when experiments are lasting more than 1/4 to 1/2 hour.

Four perforations (0.5 mm) in the rotating disc are drilled in a circular groove at about a distance of 12 mm from its edge; the groove was made in order to reduce the thickness of the disc so that the depth of the holes in the stainless steel material was only 0.5 mm. The gliding part of the disc was very carefully polished with a precision of 1/100 mm; in order to obtain a coincidence of the extraction hole and the holes in the disc (with a precision of 1/10 mm) six centering screws allowed to change the orientation of its axis in a well fixed hollow and heavy walled metal cylinder.

It will be noticed on figure 11 that a first part of the equipment consists of two chambers where the ions are first extracted and thereafter accelerated. Separating both chambers, a conical shaped wall favours the capture of the ions together with the evacuation of the gas molecules in the extraction chamber; with a rotating oil pump a vacuum of about 10^{-2} mm Hg can be maintained which is only reduced in a negligible manner when the disc rotates at the normal speed of 108 revolutions per minute. This means that the duration of

one single opening is about $1/900$ sec.

The whole system of chambers is also made of stainless steel and all insulating material is made of Teflon; this prevents all corrosion.

The pumping system connected to the acceleration chamber includes a large oil diffusion pump with a capacity of 1000 litres/sec; it is connected to a rotating pump with a capacity of $15 \text{ m}^3/\text{hour}$; this allows to maintain in the acceleration chamber a vacuum of about 10^{-5} mm Hg. A third pumping assembly (oil diffusion pump 100 litres/sec and rotating pump $6 \text{ m}^3/\text{hour}$) allows to keep a similar vacuum in the 90° deflection tube which is placed between the polar pieces of the electromagnet. The latter allows a continuous variation of the magnetic field from 150 to 3500 Gauss with a precision better than $1/50000$ when the fluctuations of the power supply are less than 5 %.

The total acceleration potential can also be modified up to a maximum value of 2000 Volts by means of a bleeder with connection to the different electrostatic lenses or electrodes which are numbered from L_0 to L_5 on figure 12.

Very soon it has been observed that the flame needed to be brought much nearer to the disc than we first thought; sufficient ions are extracted only if the distance between the burner and the disc is smaller than 8 mm when the flame length (visible cone height) is about 6 mm.

The best disposition and repartition of electrodes presented here (fig. 12) is the result of a long and fastidious investigation which very often showed to be contrary to theoretical expectations.

It seems that the best repartition and position is very sensitive to a large number of factors for which an explanation is completely impossible in the actual state of affairs. One must not forget indeed that, at each opening of the extraction hole, some unknown gas pressure gradient in the extraction chamber is established; the best conditions

for the maintainance of a sufficiently focussed ion beam are for the moment purely empirical; they depend probably also on the geometry of the chamber.

It is by placing a collector in turn after each lens (or electrode, or slit) that a progressive step for step study of the best potential repartition has been made. The same kind of difficulties occurred by choosing the best adapted size and shape of all the accelerating electrodes; these difficulties were also solved by testing the best potential by means of a collector placed each time behind each electrode in turn.

All the experienced flames were burning on a tube with conical shaped opening of 2 mm.

Since no other ion source than the flame itself could be inserted in our equipment some internal calibration had to be made on some known flame ions.

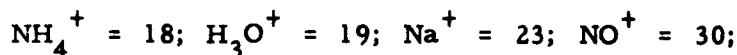
Fortunately our earlier work, where deuterium compounds were used (3), enabled us to make use of the fact that H_3O^+ forms one of the most abundant ion in many hydrocarbon flames. Furthermore it was already known that the addition of small quantities of NH_3 to rich flammable mixtures leads to the formation of a noticeable amount of NH_4^+ ions : therefore the distance between the two peaks 19 and 18 give us immediately the order of magnitude of the one-mass-difference peak distance over the whole range.

At the higher masses we could make use of the salted flames :

with Na salts	: mass 23 (Na^+)
with K salts	: mass 39 and 41 (K^+ isotopes)
with Cu salts	: mass 63 and 65 (Cu^+ isotopes)

The presence of nitrogen compounds in a flame provokes the appearance of the predominating NO^+ ion with mass 30.

To resume, the complete calibration was made possible by means of the following well defined and abundant ions :



It was observed that the resolving power of the mass analyzer was about $150 \text{ m} / \Delta \text{ m}$.

C. Summary of experimental Results :

(with the collaboration of J. Deckers, S. De Jaegere and
J. N. Bertrand)

A first remark is that there is, at least for the time being, no essential difference between the results obtained with flames burning at low or at atmospheric pressure.

Some typical results are presented in figures 13, 14 and 15 for three hydrocarbon flames. Of course the relative intensity of the peaks varies with the richness of the mixture and also with the distance between the flame and the extracting hole. Because of this it would be impossible to present here a detailed report of the large amount of data which have been obtained in our laboratory.

However there are a few observations which we have been able to make and from which important conclusions can be derived. The observations will be enounced sucessively first and will be discussed in the following section.

1. As soon as a nitrogen compound is present in the flammable mixture either as fuel (NH_3 for example) or as oxidize (N_2O for example) the most abundant ion becomes the NO^+ (7) (8).
2. Abundant ions are often the addition products of a proton and a polar molecule. This occurs for instance when NH_3 is added to the

mixture with the appearance of NH_4^+ . This explains probably the occurrence of H_2CN^+ in nitrogen compound flames, of H_2Cl^+ in halogenated flammable mixtures etc.. (7) (8).

3. The transient formation of some compounds in the flame is nicely proved when these compounds are polar molecules : in that case they appear as addition product to a proton. Some examples are : $(\text{CH}_3\text{OH})\text{H}^+$ (mass 33) (coinciding however with HO_2^+); $(\text{CH}_2\text{O})\text{H}^+$ (mass 31); $(\text{CH}_2\text{CO})\text{H}^+$ (mass 43); $(\text{CH}_3\text{COOH})\text{H}^+$ (mass 49) etc...
4. Some flames are so poor in ions that they are not detected neither by our technique of ion concentration measurement nor by mass spectrometry. Such flames are : H_2/O_2 ; $\text{H}_2 + \text{CO}/\text{O}_2$; $\text{CH}_2\text{O}/\text{O}_2$; HCOOH/O_2 ; $\text{H}_2\text{S}/\text{O}_2$; CS_2/O_2 .
5. The addition of very small amounts of an ion producing fuel to one of the preceding ion poor flames provokes the abundant production of ions and the occurrence of conductivity. This constitutes even an easy way to test qualitatively different fuels in order to find out if they are able to form ions when they are burning with oxygen (9).
6. The $(\text{CH})_2/\text{O}_2$ flame contains the following ions : NO^+ , N^+ , CO^+ , C^+ and CN^+ (NO^+ being the most abundant).
7. Addition of NO (6 %) to CO/O_2 flames does not lead to the formation of ions: on the contrary only 3 % $(\text{CN})_2$ provokes the appearance of abundant NO^+ ions.
8. In NH_3/O_2 and $\text{N}_2\text{O}/\text{H}_2$ flames the predominating ion is NO^+ .

III. MECHANISM OF CHEMI-IONIZATION (7) (9).

(with the collaboration of J. N. Bertrand, H. Philippaerts and
J. D'Olieslager)

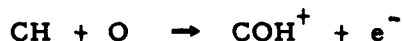
A very thorough discussion of the possible processes of ion formation by a chemical reaction in a flame has been presented by H. Eyring and collaborators in the 8th Symposium on Combustion (24) and also by H. F. Calcote (25).

Most interesting is our observation that in CH_4/O_2 and $\text{CH}_3\text{OH}/\text{O}_2$ flames ions are produced whilst in $\text{CH}_2\text{O}/\text{O}_2$, HCOOH/O_2 and $\text{CO} + \text{H}_2/\text{O}_2$ flames no ions are found. This fact proves that the process of chemi-ionization involves the reaction of a small hydrocarbon fragment containing one carbon atom which only need not to be doubly linked to an oxygen atom. It is presumably the strong exothermicity of the formation of this first double bond $\text{C} = \text{O}$ which liberates a large part of the necessary ionization energy. The fragment might be the radical CH and a possible chemiionization process would be :



which is nearly thermoneutral or slightly endothermic.

Many authors are definitely in favour of the following process which should be responsible for the primary ion production (26) :



Evidently a sufficient amount of energy is available but some problem rises concerning the observed apparent activation energy of about 50 kcalories which we have observed for the overall process of ion formation. Let us write the rate of the last process as follows :

$$\frac{dn}{dt} = k (\text{CH})(\text{O}) = k_0 (\text{CH})(\text{O}) e^{-E/RT}$$

If we admit that $E = 0$ because of the exothermicity of the proposed process we still have a relation between the concentration of radical and the temperature :

$$(\text{CH}) = K_1 e^{-E_1/RT} \quad \text{and} \quad (\text{O}) = K_2 e^{-E_2/RT}$$

and therefore

$$\frac{dn}{dt} = K e^{-(E_1 + E_2)/RT}$$

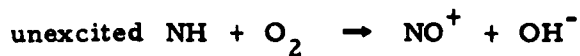
at a given mixture composition.

Now from data (10) $E_1 = 50$ kcal and, presumably, E_2 should be of the same order of magnitude so that :

$$\frac{dn}{dt} = K e^{-100000/RT}$$

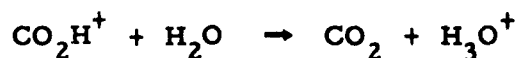
which is in complete disagreement with our observations.

In flames with nitrogen containing compounds an analogous process might be :

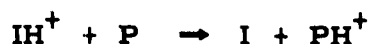


The latter being more probable.

The proton transfer to the polar molecules occurs very easily in a later stage: for instance



or generally speaking :



(IH^+ = any ion; P = polar molecule)

The following equilibrium can also be established :



Proton exchanges are distinctly noticeable when the intensity of the mass peaks are investigated at different distances between the burner and the extracting hole as illustrated in figure 16 A; all ions are disappearing in favour of the H_3O^+ which, afterwards, decays very rapidly. The existence of a small maximum in C_3H_3^+ ion peak intensity is an argument against the opinion that it would be a primary ion; C_3H_3^+ becomes more important in richer flames (curve 5). Most surprising is the observation (figure 16 B) that the decay of the ion concentration is much less rapid when a small amount of methylbromide is added to a stoichiometric mixture of $\text{CH}_4\text{-O}_2$ (N_2 50 %).

I. R. King has suggested (27) that the recombination of negative ions occurs less easier when their mobilities decrease; this of course would be the case with the heavy Br^- taking the place of the lighter OH^- . It is still hard to understand why the presence of negative ions should reduce the rate of recombination except if one admits that in any case the recombination occurs by some dissociative process as for instance :



If so it is quite understandable that the frequency of the process $\text{H}_3\text{O}^+ + \text{Br}^- \rightarrow \text{H}_2\text{O} + \text{HBr}$ because of the much smaller mobility of Br^- as compared to the mobility of the electron.

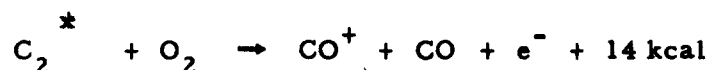
The decay of thermal ions (K^+) is very much slower than the decay of chemiions; it goes parallel with the cooling of the burnt gases (figure 17); the addition of N_2O leads to the formation of NO^+ which

is definitely a chemiion.

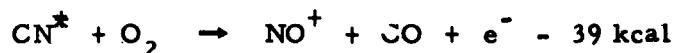
As soon as NO molecules are present in the burnt gases charge transfer occur because of the low ionisation energy of NO :



There is still a problem concerning the formation of the ions in the cyanogen flames; in this case of course no CH or NH radicals are formed in the reaction zone. However excited C_2^* are produced which are able to react according to :



There is also another possibility :



This last reaction would mean that the formation process of the ions occurs with an activation energy which is the sum of 39 plus the activation energy of the formation process of the excited CN^* radical :



However the presence of ions in a CO/O_2 flames with additives such as CCl_4 or C_2Cl_4 would indicate that the process involving C_2^* is more likely; indeed, the addition of these halogenated compounds is accompanied by a marked C_2^* emission in the flame.

The short discussion resumed here above shows that some light is yet thrown on the problem of chemiionisation although many points remain still obscure. However, as compared to the situation existing only a few years ago, it may be assumed that the final solution is to be found by continuing the study of the ions identity in flames which differ widely in the nature of the constituting atoms.

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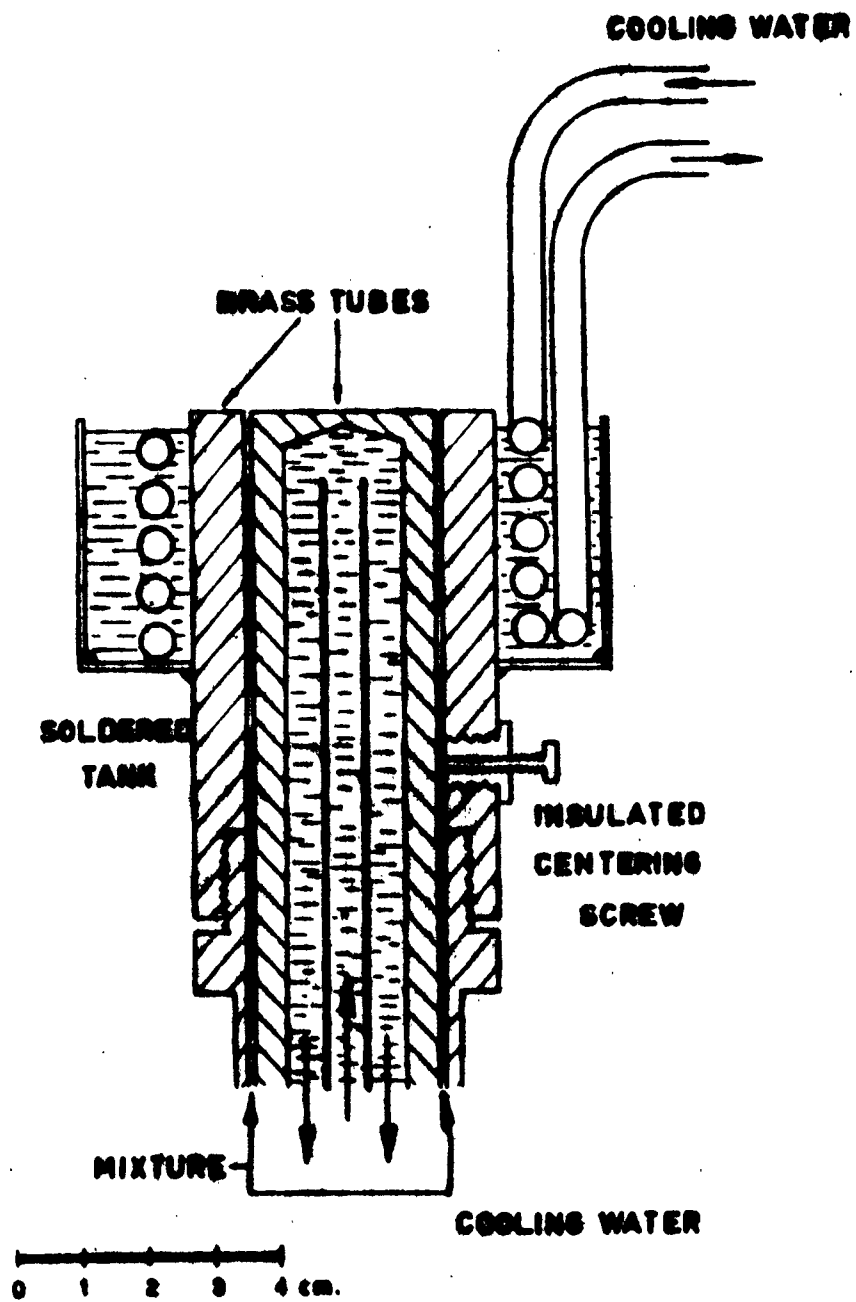


Fig. 1.

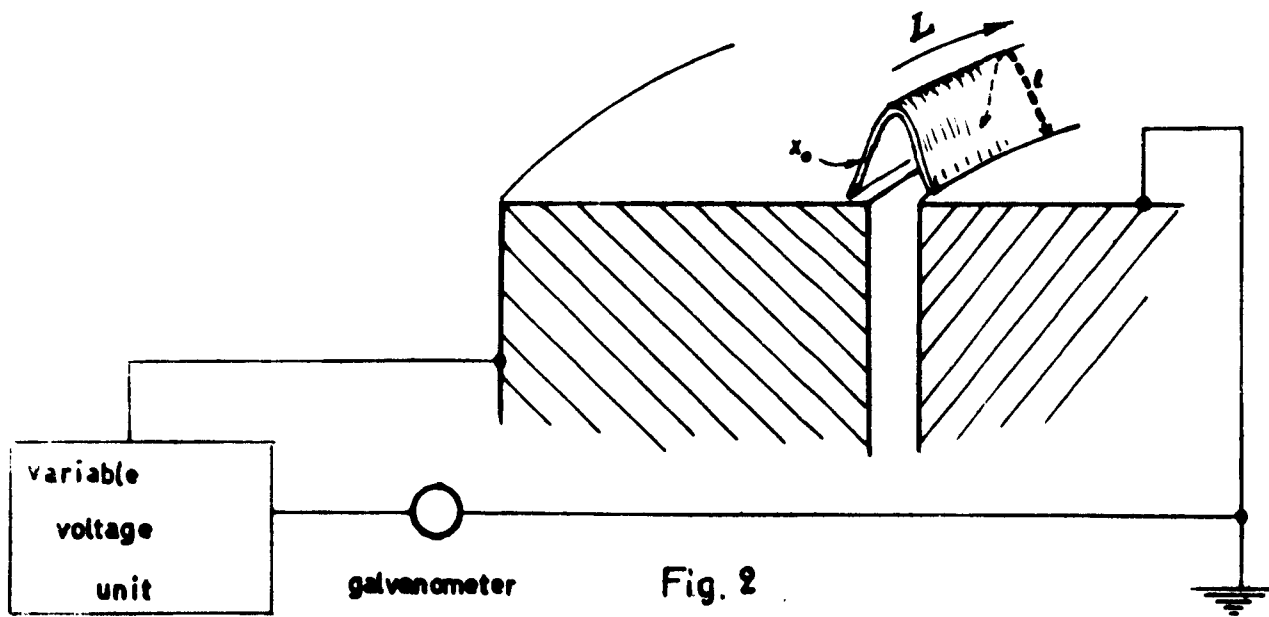
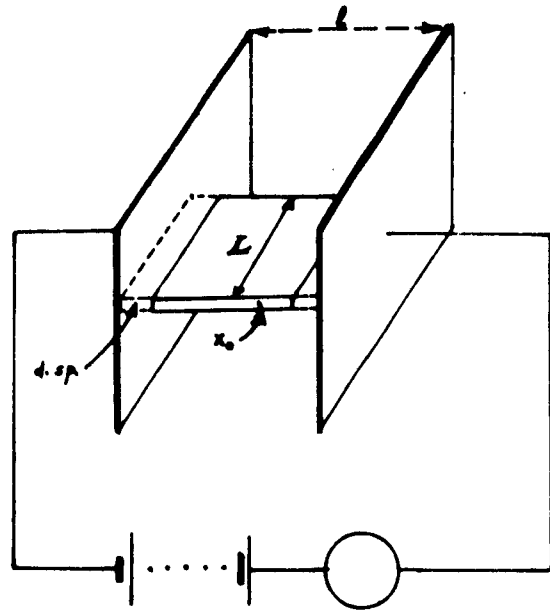


Fig. 2

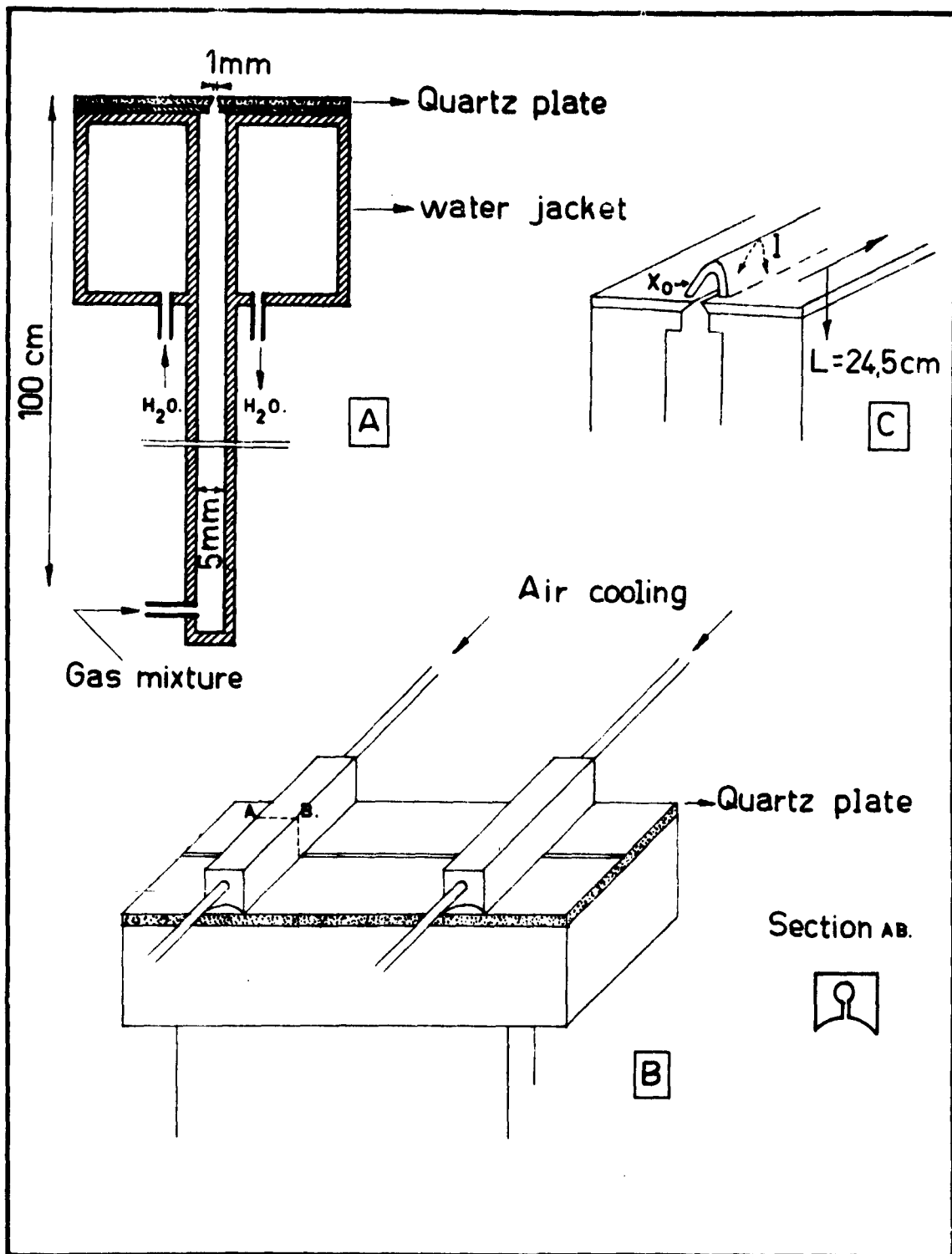


Figure 3

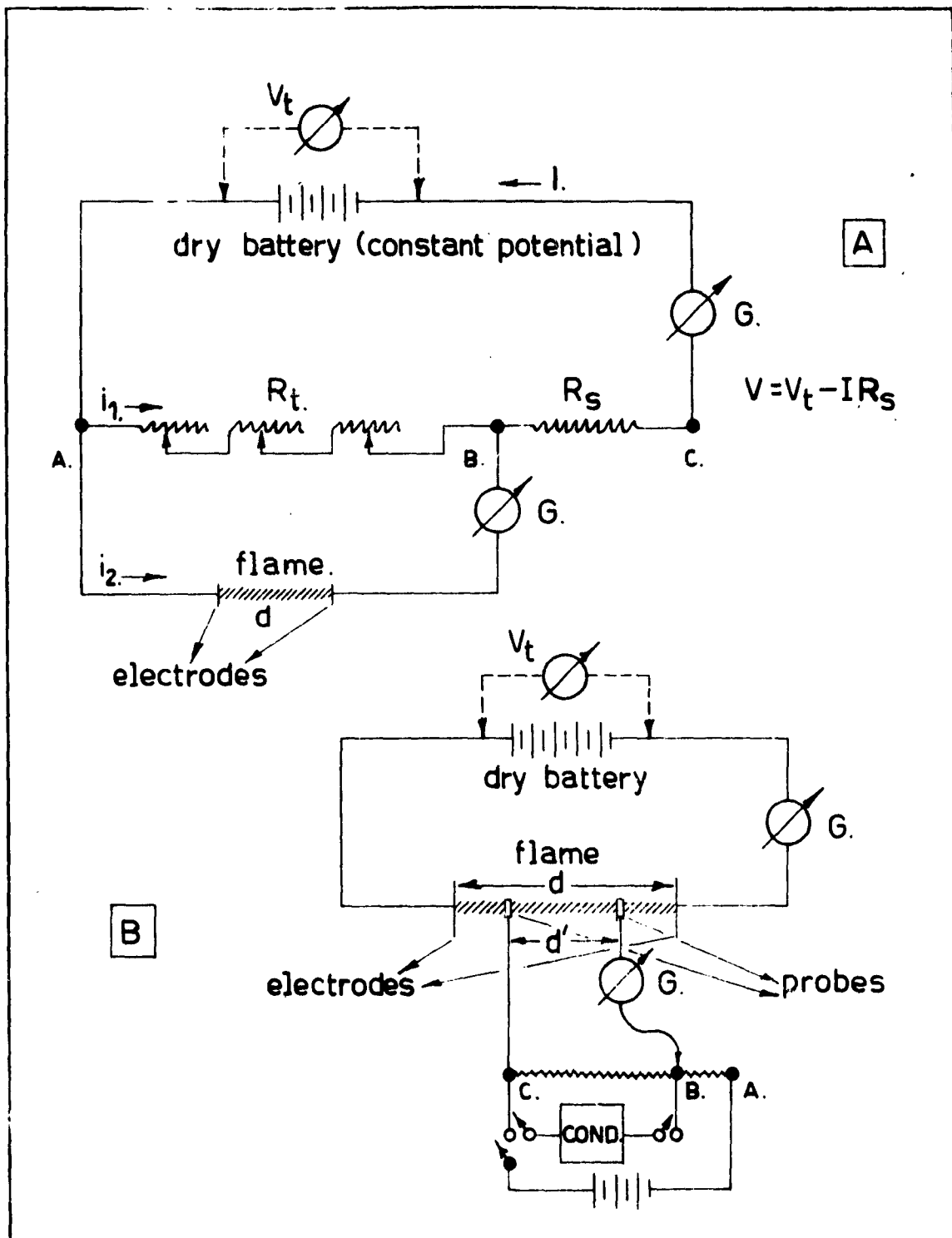


Figure 4.

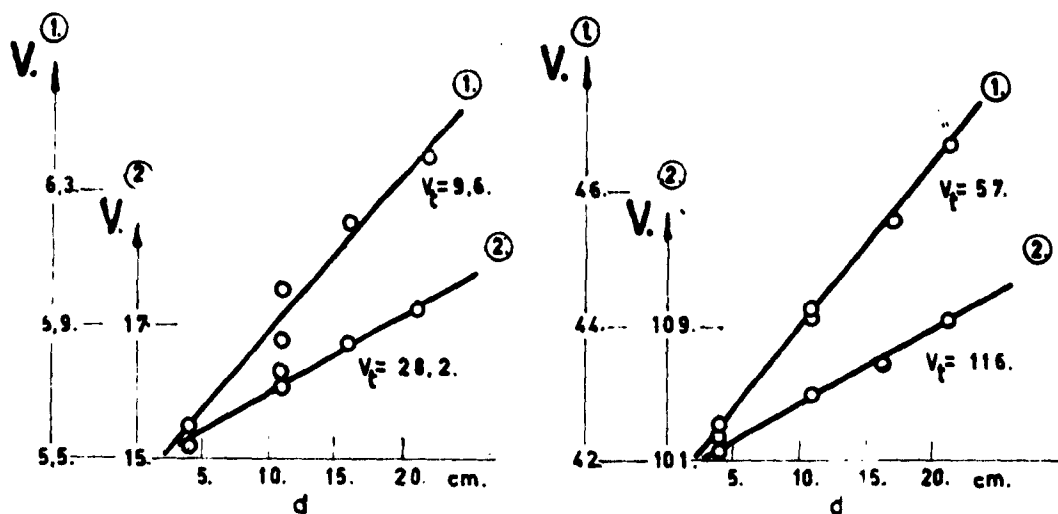


Figure 5A ($V = V_t - IR_s$; see fig. 4A)

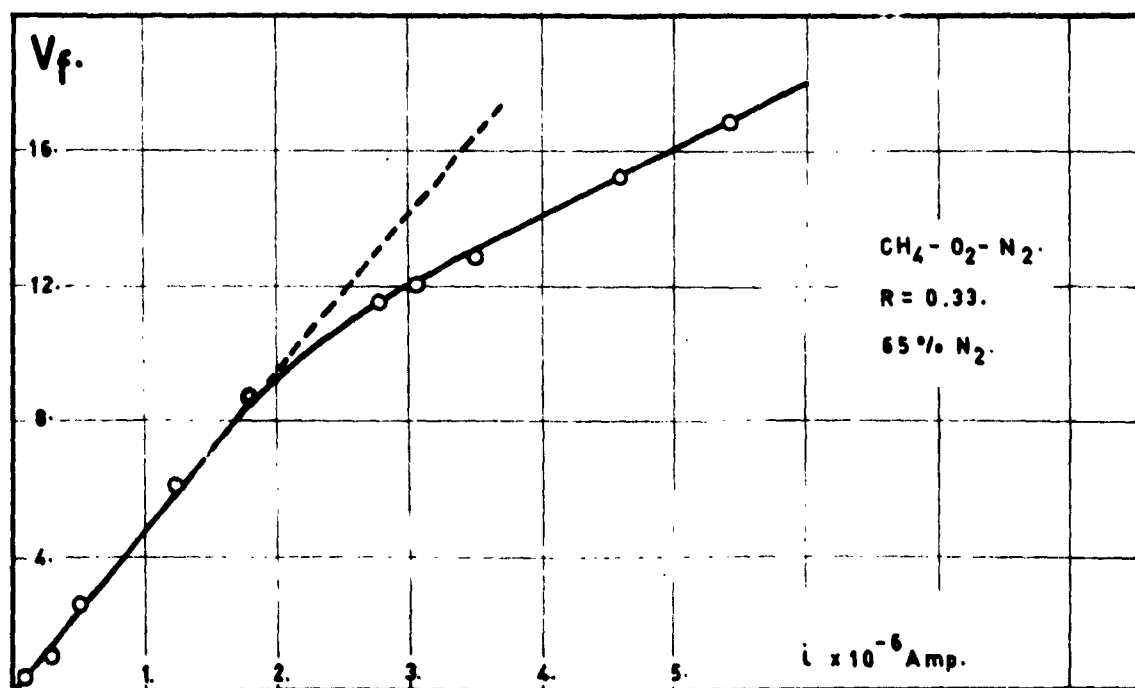


Figure 5B

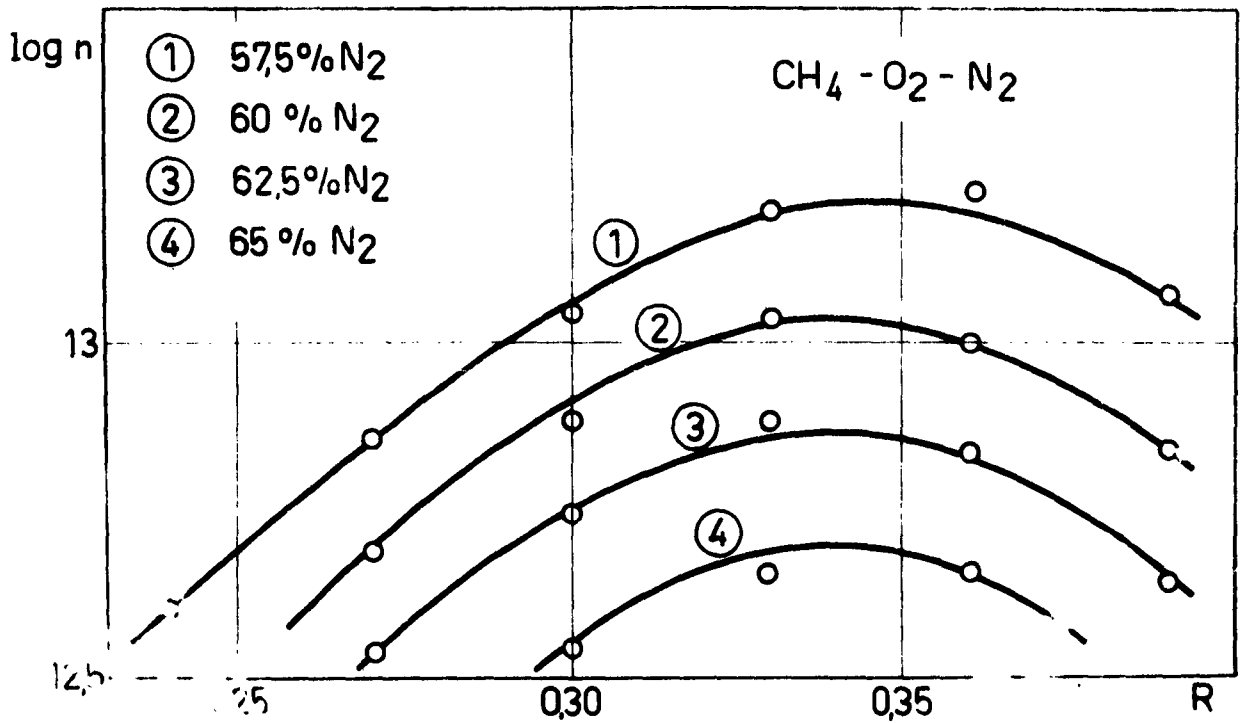


Fig.6.

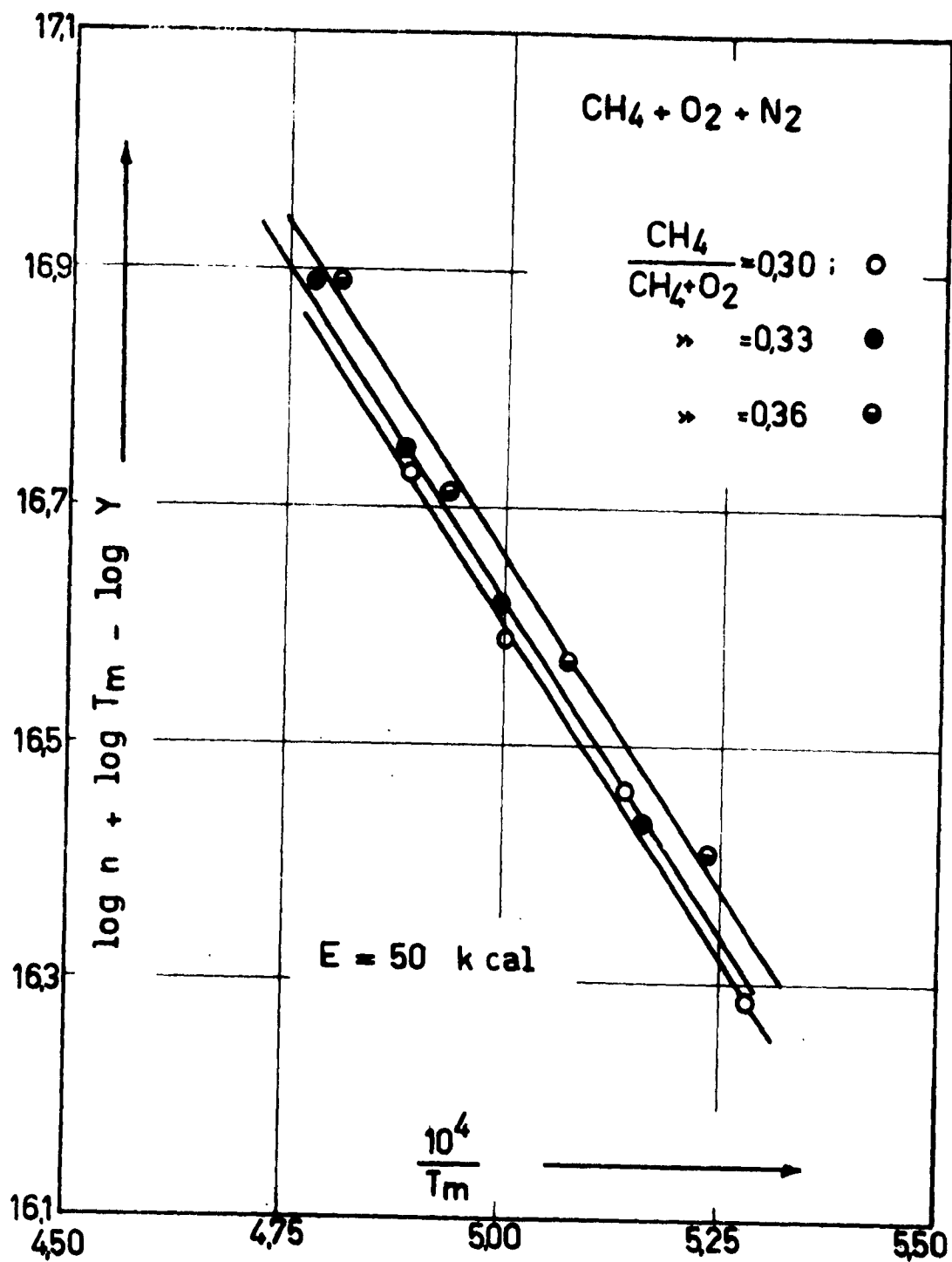


Fig.7.

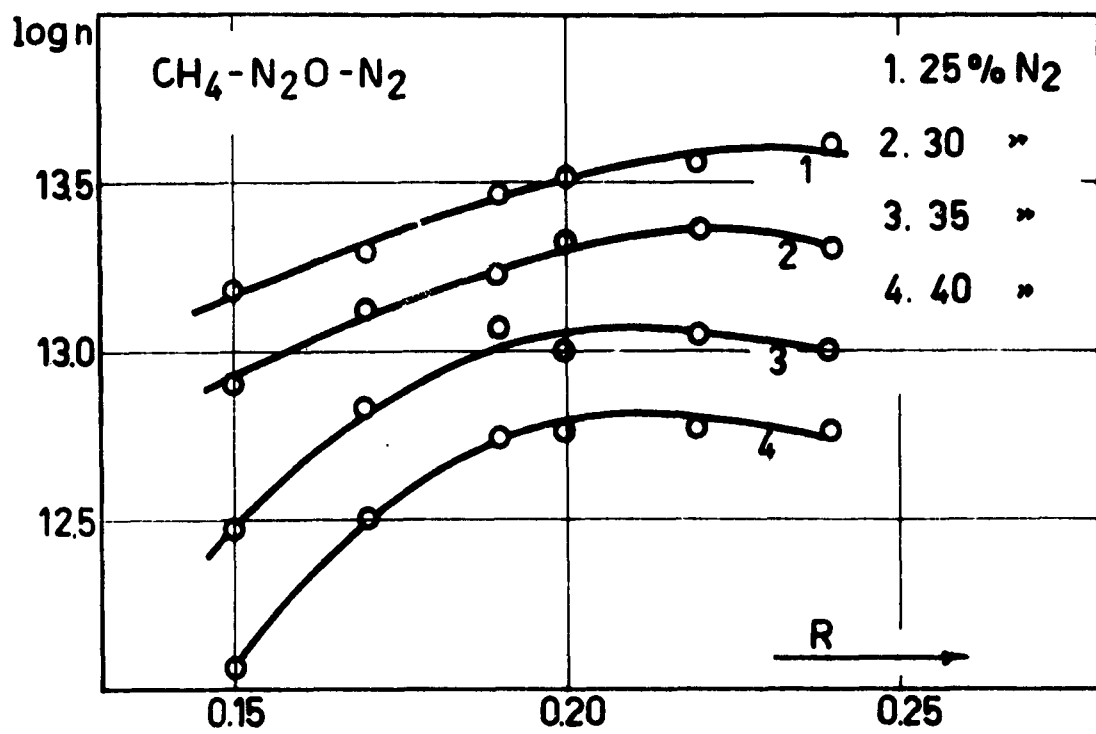


Fig. 8.

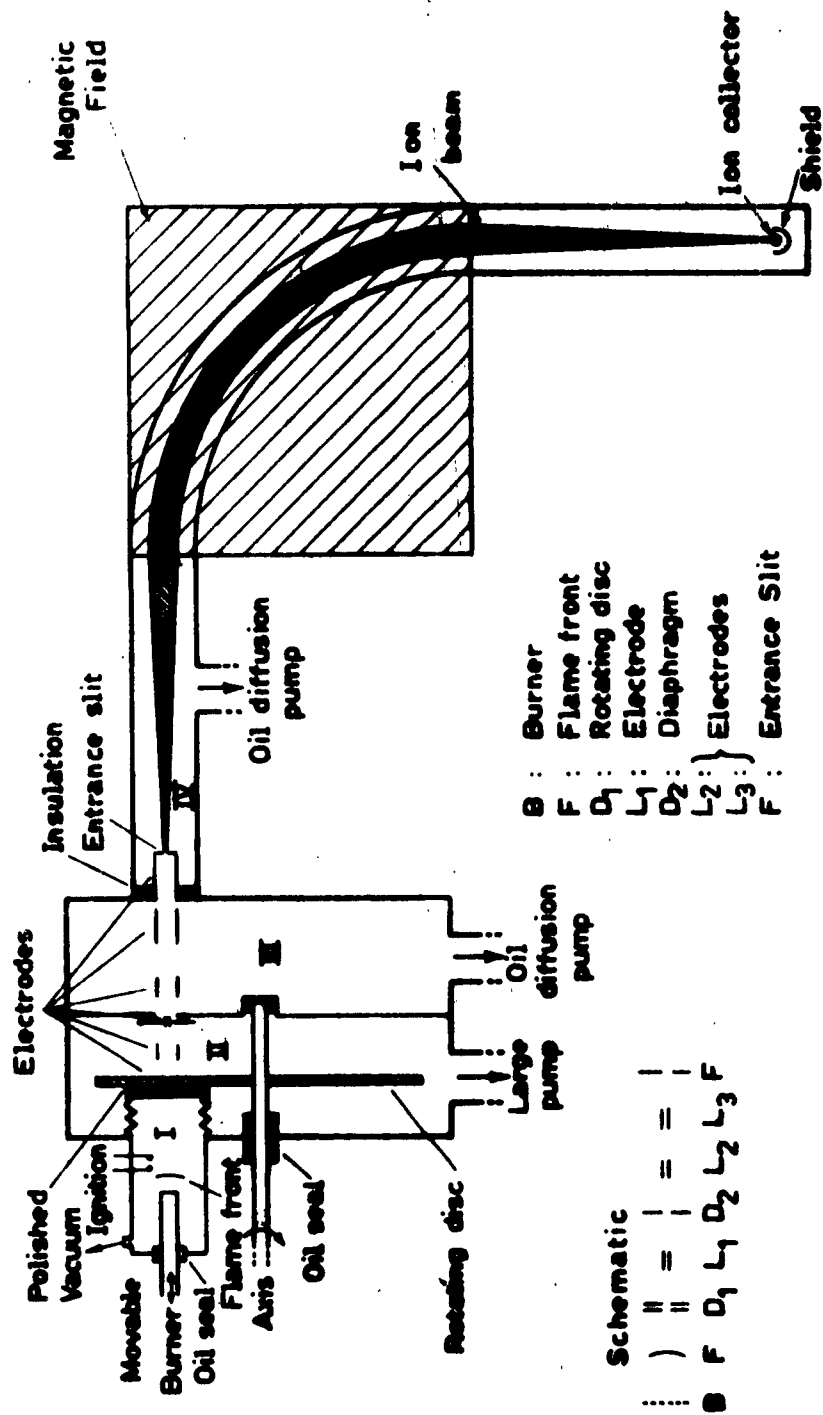


Fig. 9.

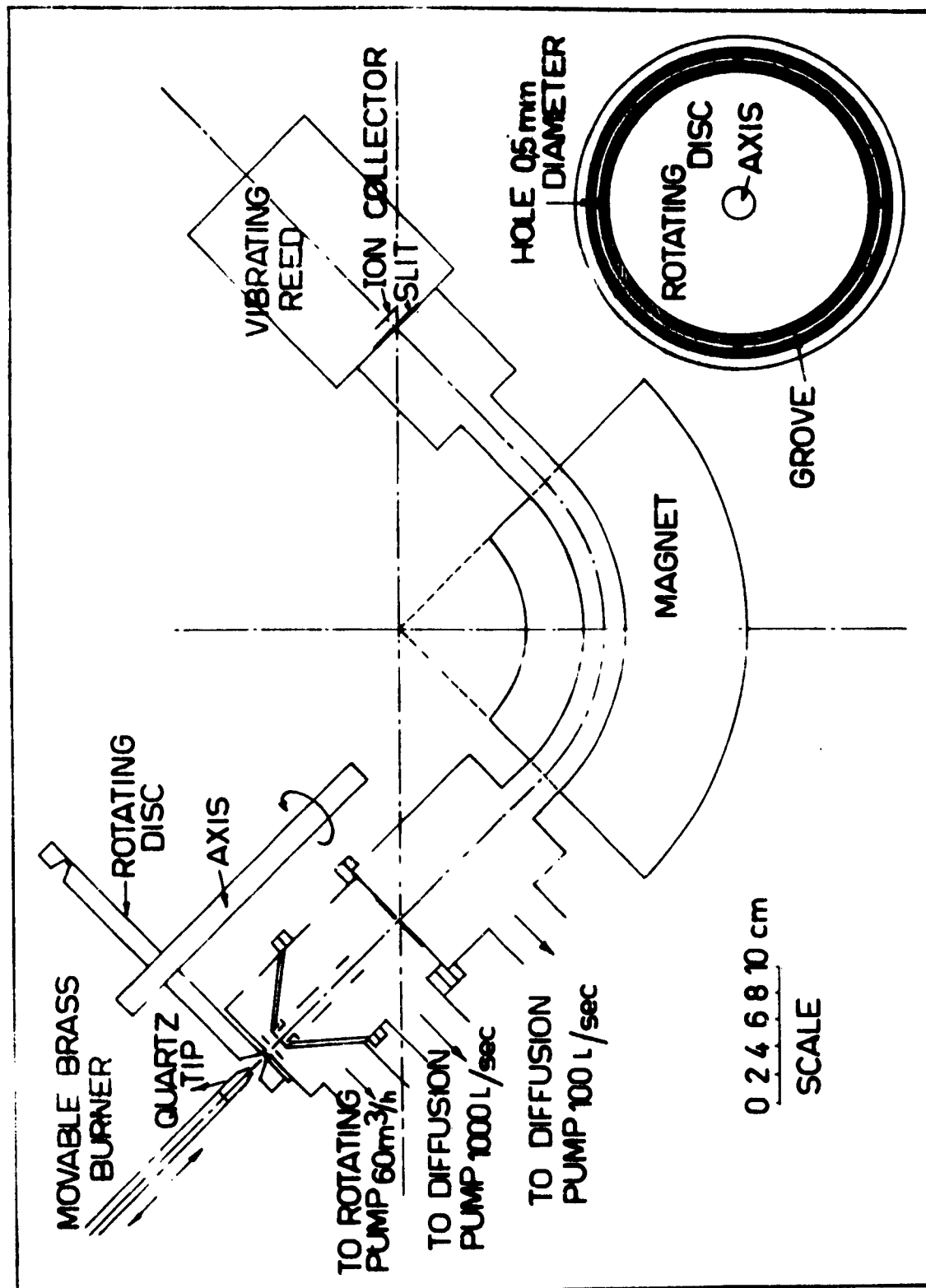


Fig.10.

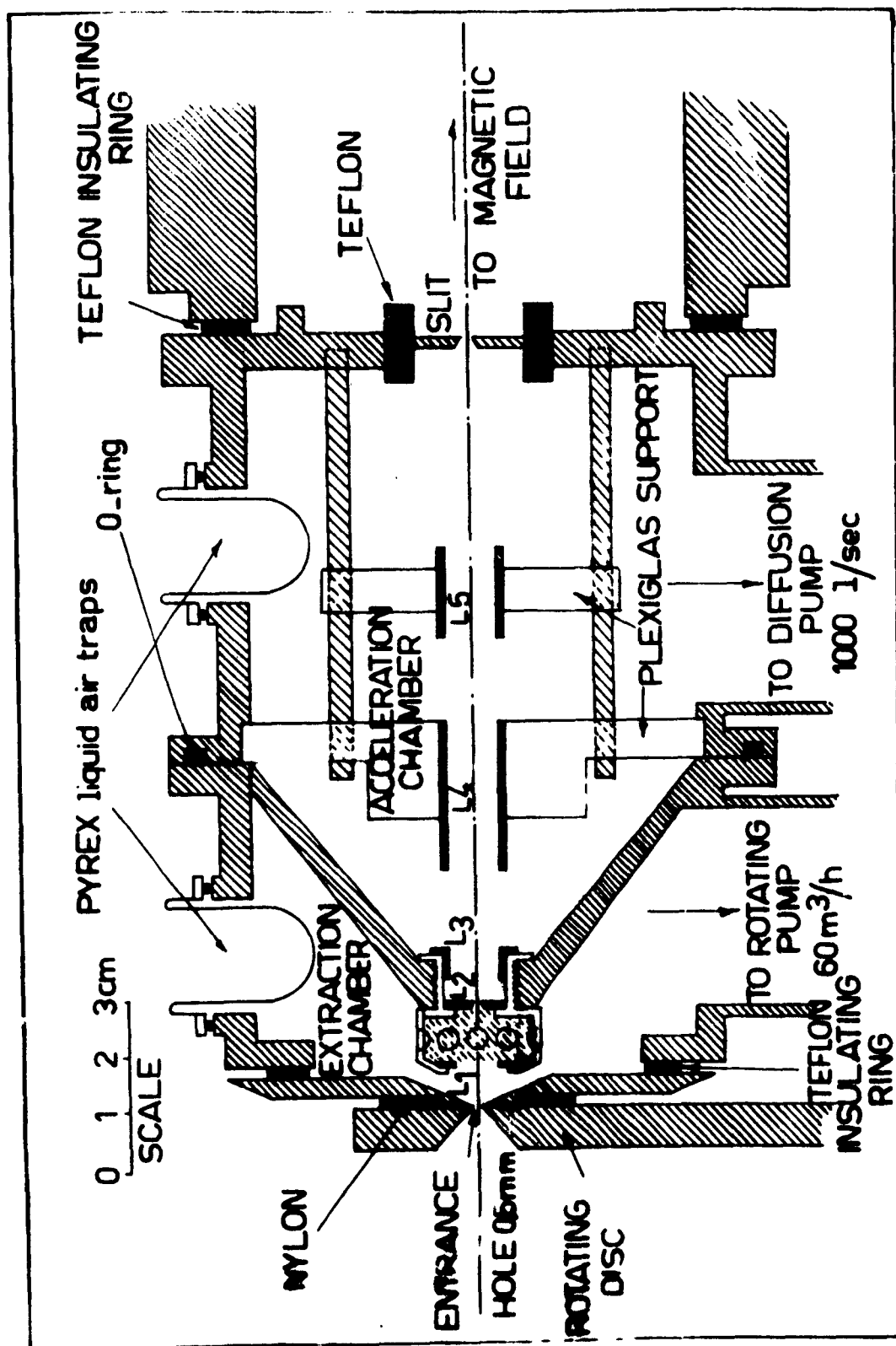


Fig.11

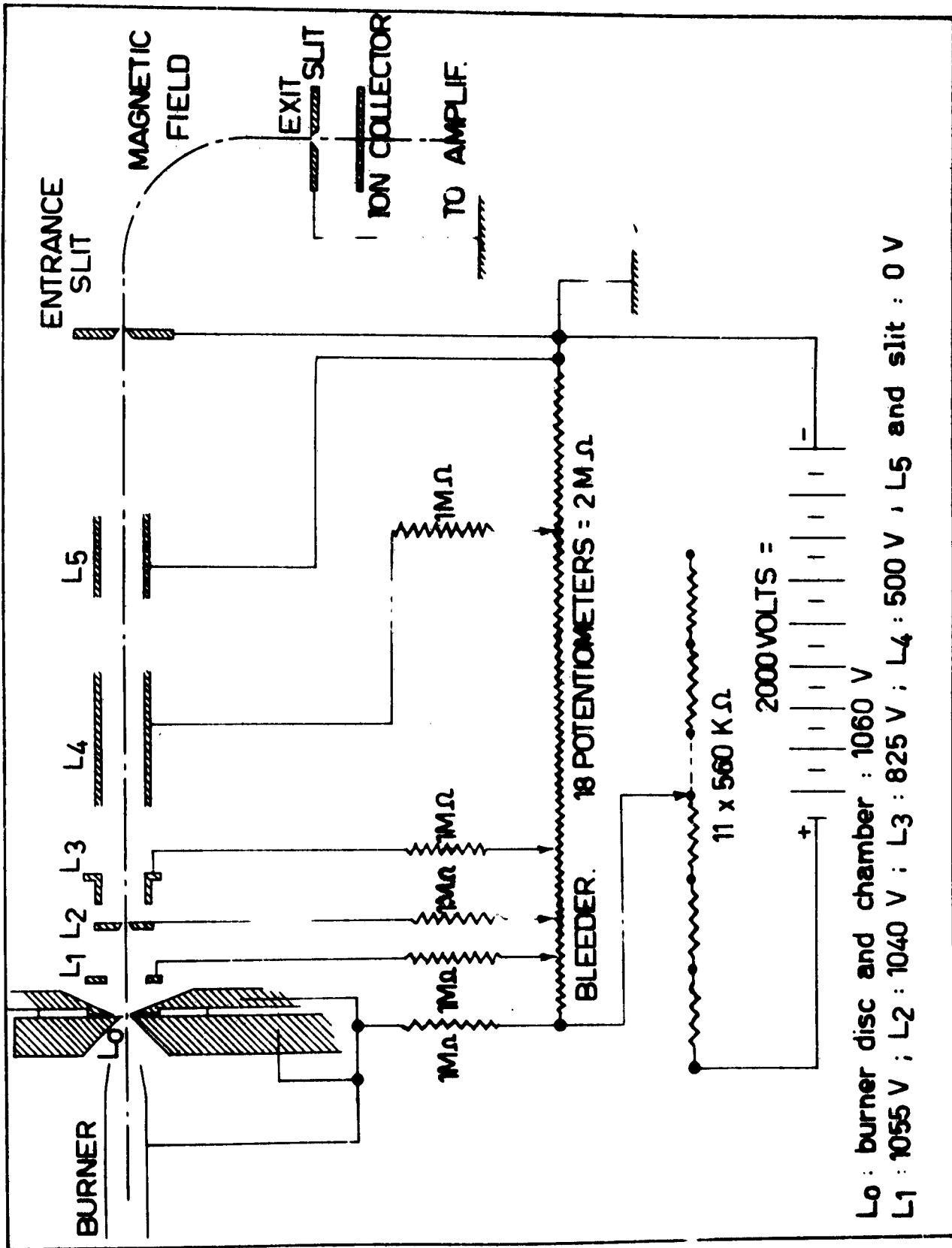
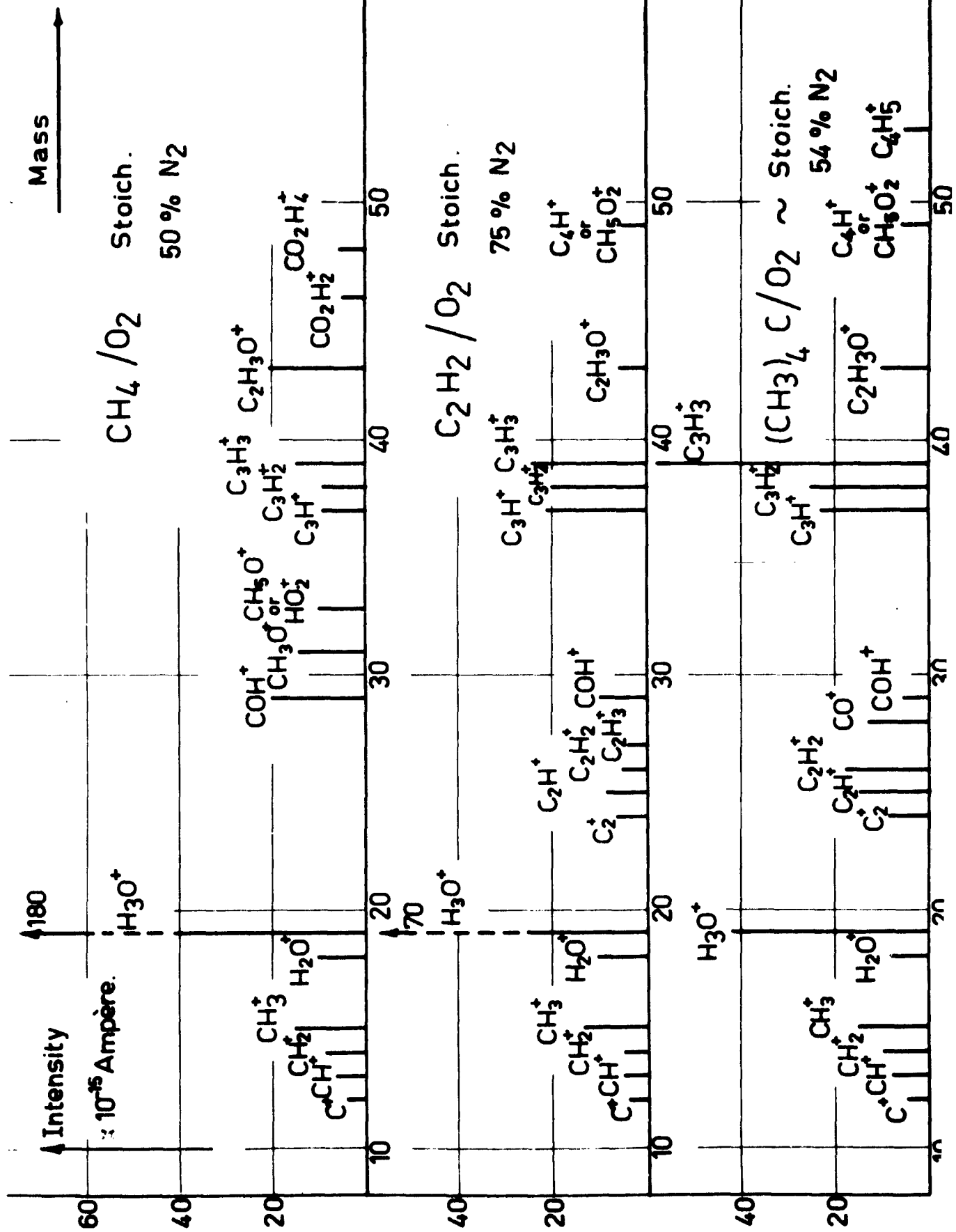


Fig.12.



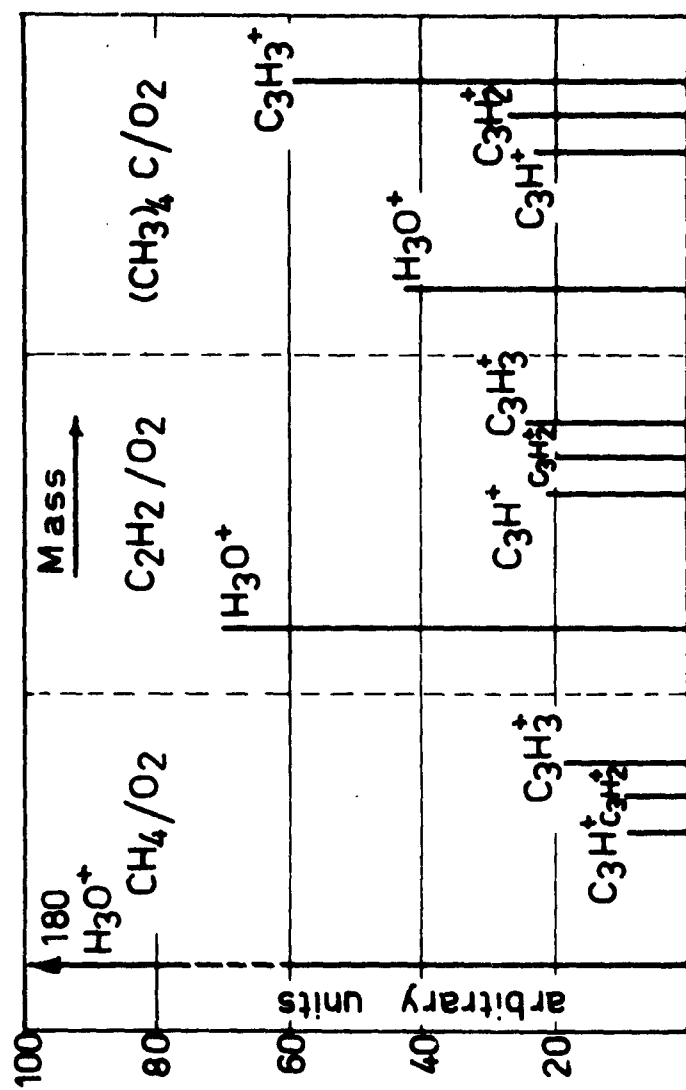


Fig. 14.

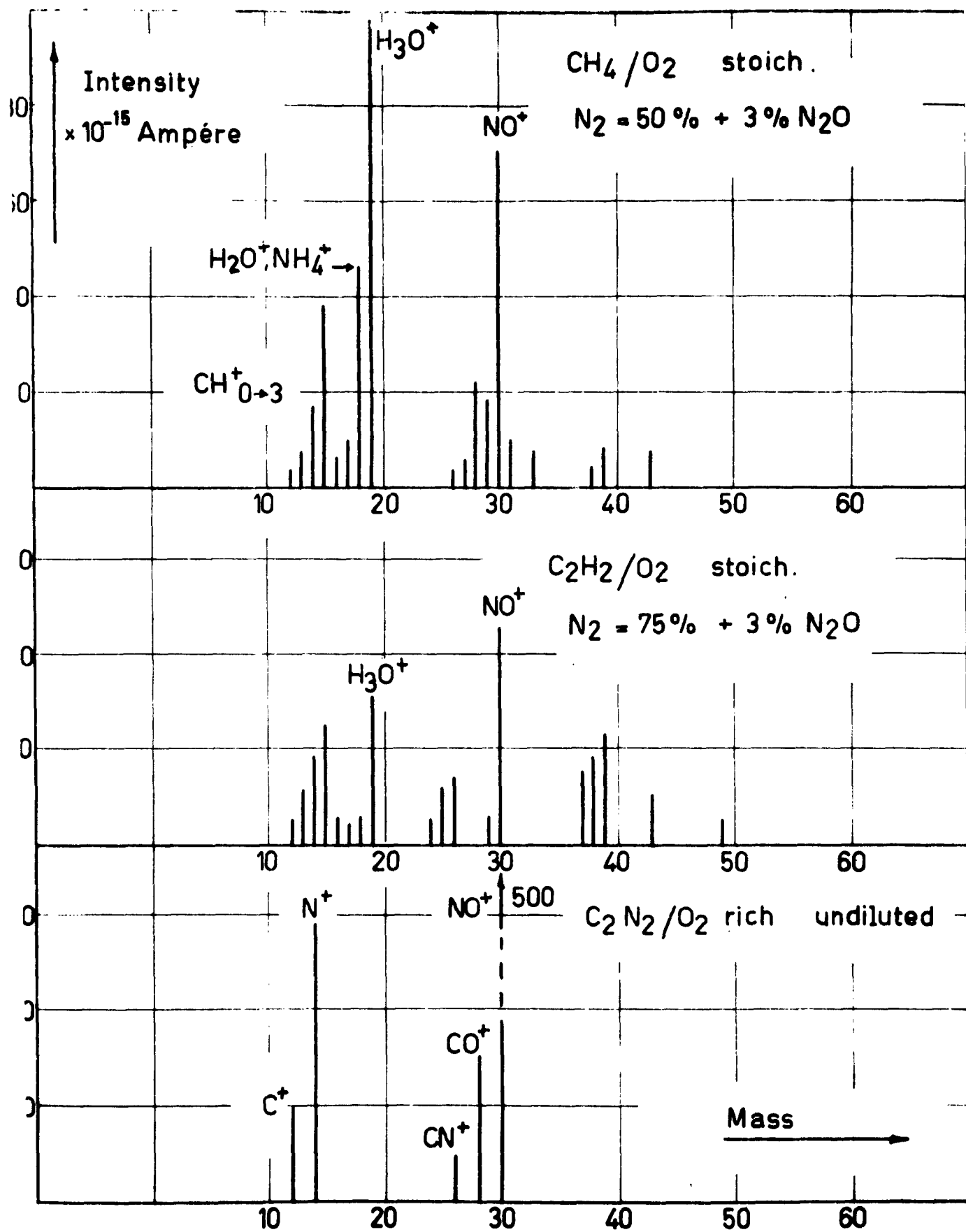


Fig. 15.

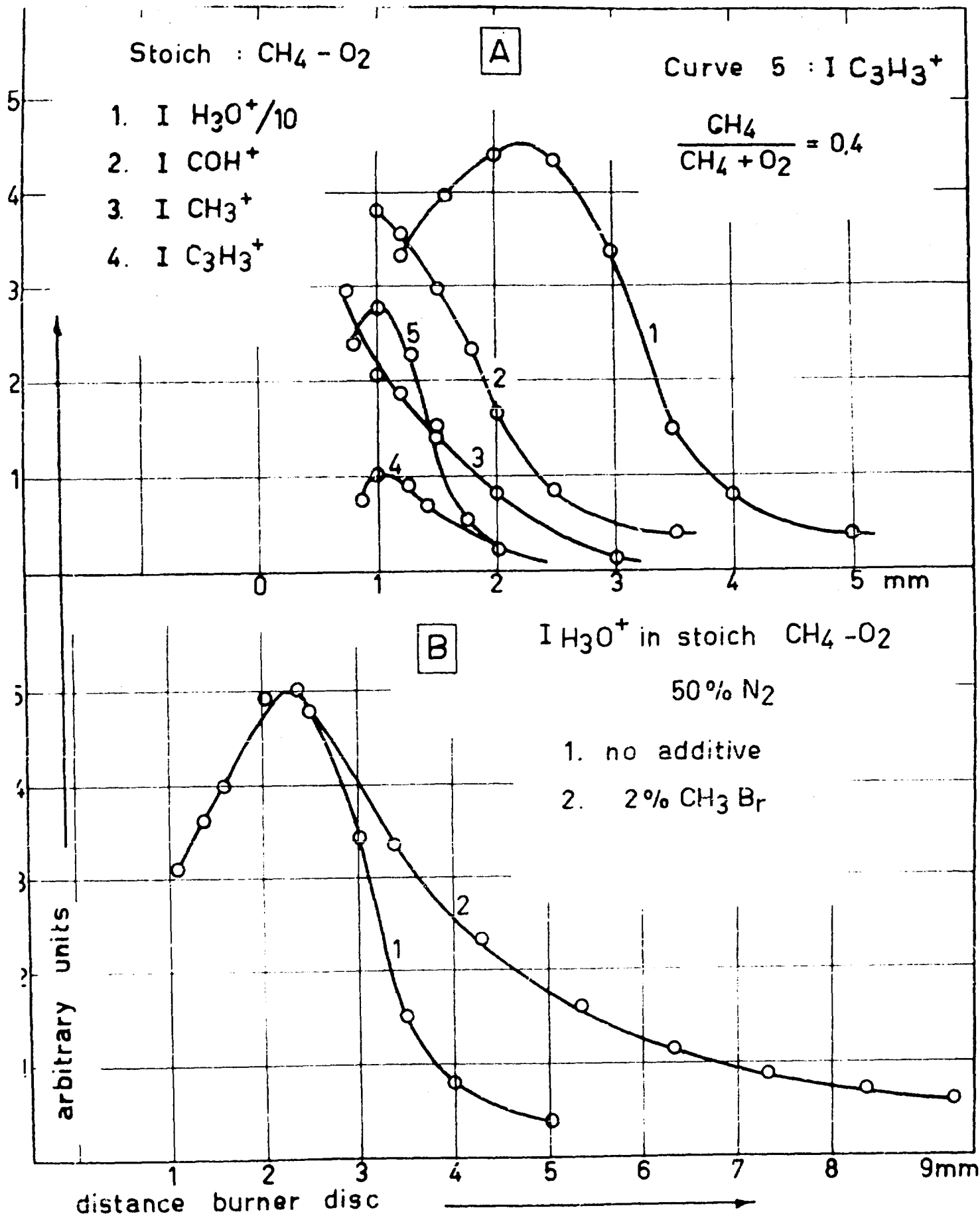
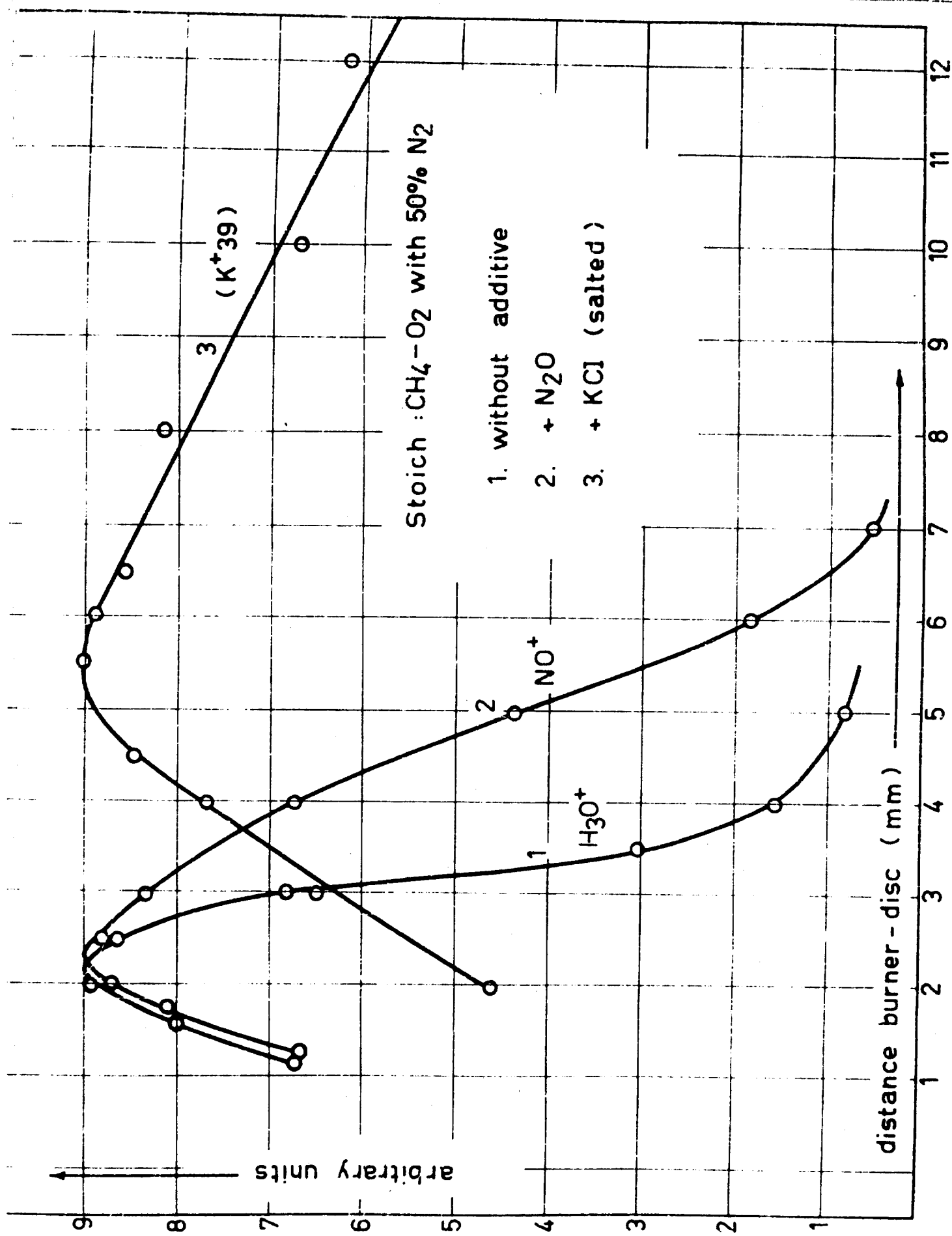


Fig. 16.



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